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7. Abstract

This document provides a guideline for methods of assessment of hot cell screening instrumentation, particularly Raman spectroscopy based systems. Development of this system is concurrent with testing of probes, fiber optics, laser sources and spectrometer components for eventual deployment in waste tanks. Screening within the laboratory process environment should reduce sample load and analysis cost for high level waste samples destined for analysis at the 222-S Analytical Laboratory.

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LIST OF FIGURES

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LIST OF TERMS

ASTM	American Society for Testing and Materials
CCD	charge coupled device detector
ED	Engineering Development
FSU	Florida State University
HLW	high level waste
IC	ion chromatography
ICP	inductively coupled plasma spectroscopy
LT	laboratory technology (procedures)
NIST	National Institutes of Standards and Technology
PAL	Processing and Analytical Laboratories
PCL	Process Chemistry Laboratory
PDSU	Process Development Support Unit
PNL	Pacific Northwest Laboratories
NIST	National Institute of Standards and Technology
RMW	radioactive mixed wastes
rms noise	root mean square noise
SST	single shell tank
TFO	Tank Farm Operation
TOC	total organic carbon analysis
USQ	unresolved safety question
WHC	Westinghouse Hanford Company

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1.0 INTRODUCTION

A feasibility study for the use of Raman spectroscopy to provide analytical screening data on Hanford waste tank constituents was performed by Florida State University (FSU) in FY92. The results of that study are documented in *"Detection and Quantitative Analysis of Ferrocyanide and Ferricyanide,"* WHC-SD-TD-RPT-003, Revision 0, Westinghouse Hanford Company, Richland, Washington (WHC 1992). In summary, this study showed that the detection limits of a Raman spectroscopy system were sufficient to provide valuable data on ferrocyanide and ferricyanide salts and selected oxyanions in tank wastes. These tests were performed on waste simulants and pure materials.

With the successful completion of this investigative first phase, the next step towards the routine use of this tool in an operational environment, is to investigate the Raman spectra of actual waste tank material and compare results to waste simulants. The information and knowledge gained on the system during the feasibility study will be used as the baseline for analysis of the waste tank material spectra. This includes calibration, optimization, and baseline pure material spectra.

The experience and knowledge gained from taking and analyzing the spectra of actual waste tank material can then be used to proceed with development of this system for routine use as an analytical tool. At this point in time it will only be possible to defensibly determine the chemical identity of components by peaks of species which have been assigned during the feasibility study (i.e. only those peaks which have reference spectra on pure materials). It is anticipated that there will be much more information in the waste tank material spectra than can be determined in this way.

The purpose of this document is to guide development and assessment of laser Raman spectrometric methods for semi-quantitative analysis of anions in high level waste (HLW) samples in a hot cell. The hot cells in room 1E of the 222-S Laboratory will be used as a test bed. After successful demonstration of the equipment and methods, procedures may be written for routine use of the screening tool for determining the minimum analysis requirements for waste tank core segments as they come into the laboratory.

Specific operations and performance assessments which are unique to the hot cell environment include use of a silicon charge coupled device (CCD) detector in a radiological environment, cleaning and verification of cleanliness of probes, positive reproducible peak identification in samples that may fluoresce or provide maximum background or matrix interferents and definition of homogeneity in real-tank wastes.

Technology developed under this plan may be combined with other screening technologies which are being developed such as remote infrared spectroscopy and radionuclear spectroscopy. These "on-the-spot" analyses will ultimately guide compositing and subsampling activities at the point of extrusion. Spectroscopic and radionuclear screening, probe positioning and tracking, and chemometric data analysis performed within the laboratory process environment can dramatically reduce the sample load and analysis cost for HLW samples at the 222-S Analytical Laboratory.

These technologies are also recognized as having potential for application to in-situ analysis of HLW tanks. The hot cell provides a logical test bed for evaluation of possible future applications. In addition, enhancement of analytical capabilities to analytical services within the 222-S Laboratory and reduction in sample turn-around is expected to be realized within two years, with initial deployment in the hot cell in Fiscal Year 1993.

2.0 OBJECTIVE

The work described in this document will provide an initial technical assessment of a Raman spectrometer optically interfaced to a hot cell. Specifically, oxyanions and ferrocyanide anions will be identified qualitatively in real tank matrices; a semi-quantitative analysis of these anions based on nitrate concentrations found in these wastes will be performed; and system assessment will be provided to direct further development such as routine operation and application of the technology to waste characterization. Additional work described in this document fulfills requirements set by the waste tank safety program in support of the ferrocyanide unresolved safety question (USQ). Specifically, this work provides for semiquantitative analysis of ferrocyanide species as developed by FSU using remote Raman characterization. This quantitative work is performed directly on tank waste samples and involves no sample preparation. This direct analysis has potential application as both a sample screening tool in the laboratory and as a means of in-situ characterization in waste tanks.

The preliminary hot cell tests will involve tests with actual waste samples obtained from up to three Hanford waste storage tanks (241-T-107, -C-111, and -BY-104; samples from tanks T-107 and BY-104 are available; a sample from C-111 is subject to possible changes in tank sampling plans). These tests will include benchmarking with non-radioactive samples in both a controlled cold laboratory environment and in the hot cell. These tests will utilize known pure compounds and constructed waste tank or process simulants available from the laboratory. These simulants will be analyzed by independent methods at a laboratory outside WHC.

The tests include the following:

- Comparison of system performance in a controlled environment and the hot cell on pure compounds.

- Comparison of results from peer-analyzed surrogates in controlled and hot cell applications.

- Comparison of results obtained on real wastes with analyses available from the laboratory.

- Comparison of surrogates with real tank wastes.

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3.0 SCOPE

This document covers the actions required by the Westinghouse Hanford Processing and Analytical Laboratories (PAL) and Engineering Development (ED) groups in preliminary evaluation of a remote Raman screening system in the 222-S hot cells.

In addition it provides the basis on which additional development and investigation work on Raman Spectroscopy for analysis of Waste Tank Materials will be conducted.

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4.0 PERFORMING ORGANIZATIONS AND ACTIVITIES

This work represents a team effort between Westinghouse Engineering Development and the Processing and Analytical Chemistry Laboratories. Processing and Analytical Laboratories will be responsible for performing the tests outlined in this plan. This includes responsibility for setup and operation of the system at the 222-S Laboratory Hot Cell and subsequent analysis of the gathered data. Quality assurance protocols under normal laboratory procedures will be adhered to during the testing. Engineering Development will be responsible for establishment of the overall program direction and review of test plan and results. It is anticipated that Pacific Northwest Laboratory (PNL) will be utilized for consultation and peer review of test performance and results. Additional work in FY '94 will proceed between the WHC laboratory and PNL laboratory with collaboration and report generation.

All work will proceed according to the items in the attached schedule. Results from tests, calibrations, optimization protocols and spectrometer use will be recorded in laboratory notebooks. A final report will be issued from the laboratory describing key observations and data comparisons (see schedule for deliverables).

PROCESSING AND ANALYTICAL LABORATORIES	1)	Set up and operate Raman instrument at Hot Cell.
	2)	Operate hot cell manipulators, extruders and core processing equipment.
	3)	Perform evaluation and chemical measurement assessment and testing as applied to sample processing.
	4)	Develop Hot Cell procedures.
	5)	Provide technical expertise for analytical instrument development and operation.
	6)	Design and build chemical standards for chemical assessment.
	7)	Develop hot cell test plan.
	8)	Perform system optimization and quality assurance protocols
	9)	Collect and interpret screening data.
222-S FACILITY HEALTH PHYSICS	1)	Provide radiation monitoring in support of operation of hot cell and sample handling.

ENGINEERING DEVELOPMENT	1)	Manage tank deployment program and interaction with hot cell screening.
	2)	Provide engineering support for hot cell instrumentation and screening equipment.
PROCESS DEVELOPMENT SUPPORT	1)	Perform conventional sample analysis on single shell tank (SST) waste.
	2)	Provide data as available or on request for the tanks being screened.

5.0 DEFINITIONS AND ABBREVIATIONS

5.1 DEFINITIONS

The following definitions are used in description of extruded tank wastes and may appear in this document or reports generated as a result of these tests.

Blend/Blending - The mixing together of proportional subsamples of different segments and/or parts of segments, also referred to as compositing.

Blend Plan - A strategy describing the amount of each segment or part of a segment to be combined to arrive at a representative composite sample.

Cell Constants - Parameters which may contribute to an analytical measurement of a sample cell such as cleanliness, optical characteristics, and pathlength.

Composite/Composite Sample - A collection of portions of individual units blended together to make a representative sample of a larger unit. The individual units may be either whole segments or parts of segments. The larger unit may be either a whole core or an individual stratum within a core.

Core - A set of segments taken in succession from the same location that give a vertical (stratigraphic) representation of a waste tank at that location.

Cubicle - A shielded hot cell in which highly radioactive materials are handled remotely by manipulators.

Extruder/Extruder Jig - The device which holds the segment sampler and pushes the segment sample out onto a tray.

Extrusion - The process by which a segment sample is taken out of a sampler.

Facies - A facies is a region of waste, not longer than one segment. A facies is a visually differentiable part of a segment. A facies may be a part of a stratum that is bigger than the segment or be a stratum by itself. If a segment appears uniform throughout, then the entire segment is one facies (see Figure 5-1).

Homogenization - The process of making a composite or an individual facies uniform throughout.

Homogenized Segment/Facies - A sample which has been mixed together to the point of being uniformly mixed and thus representative of the entire segment or facies.

Hot Cell - (see cubicle)

Qualification Plan - A document addressing validation and verification protocols and documenting requirements that must be addressed to support system performance, accuracy and precision and methods of chemical data validation.

Sampler/Core Sampler/Segment Sampler - The device in which a waste tank core segment is taken. It is a device which is lowered through the drill string to obtain a vertical sample of waste in a single location in a waste tank.

Screening - The process of comparing analytical measurements of segments of tank wastes with other segments and subsections within the same segment.

Segment/Core Segment - The individual units that make up a core sample. A segment is the entire amount of material recovered from the tank by one sampler. It can hold material up to 48 centimeters (19 inches) in length.

Simulant - Synthetic waste materials that are made up from process flow sheets and known tank compositions to ideally mimic the contents of specific tanks and processes.

Stratum - A contiguous portion of a tank's contents that has similar properties throughout. A stratum may be represented by a single segment, a facies in a segment, or several contiguous segments and/or facies.

Surrogate - Mixtures of waste materials that are made up of well understood chemical components that have been analyzed for final chemical composition. These materials do not necessarily mimic the compositions of specific tanks.

Figure 5-1.   Stratigraphy of Cores.
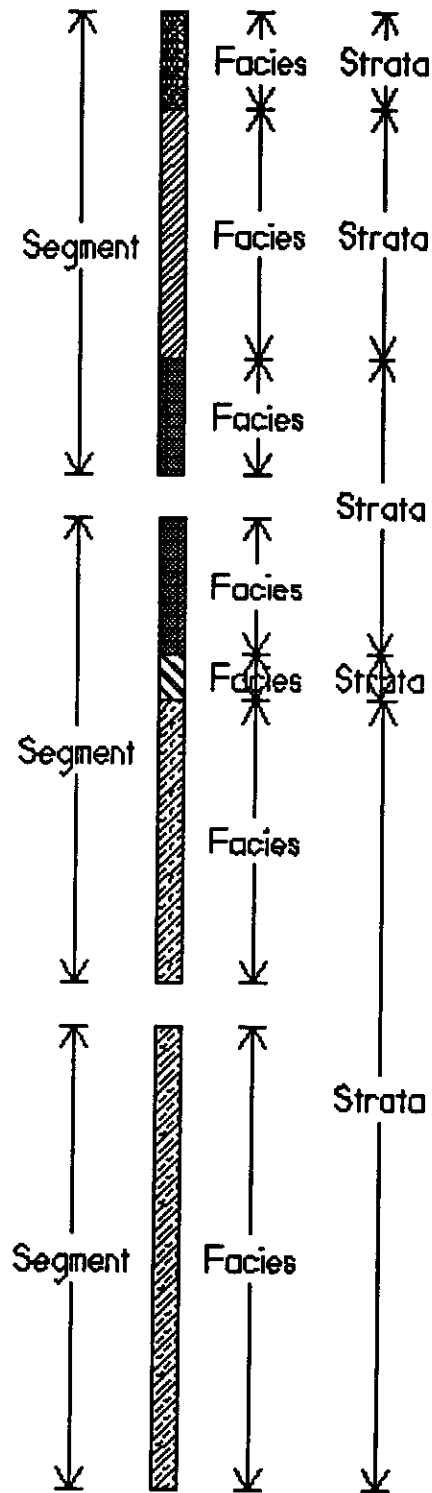
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6.0 DESCRIPTION OF RAMAN SCREENING SYSTEM

The complete Raman scanning system consists of a dispersive, single stage spectrometer with interchangeable gratings. An argon ion laser or a diode laser source, silica fiber delivery system with a tapered tip and predetermined focal plane, a liquid nitrogen cooled CCD detector and a computer. This system will be placed in an isolated box to prevent contamination and release difficulties once the system enters the laboratory. A diagram of the proposed system at the hot cell is provided in Figure 6-1.

Raman spectroscopy is a vibrational form of spectroscopy that provides information complementary to infrared spectroscopy on molecules. Unlike infrared spectra which result from direct absorption of infrared light, Raman spectroscopy is the result of inelastic light scattering. Therefore, there is no wavelength dependence on the source of excitation radiation. Instead the light frequencies shifted from the source frequency for a given molecule are observed. The resultant spectra are obtainable with laser excitation ranging from the ultraviolet to the near infrared. This makes Raman based techniques ideally suited for application with fiber optics, as the source frequency can be tuned into favorable light transmission ranges for various materials. In addition, water is a weak scatterer of Raman shifted light. This makes Raman spectroscopy suitable for aqueous samples and slurries.

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Figure 6-1.   Hot Cell Raman Spectroscopy System.

F – Optical Filter
L – Optical Lens
CCD – Charge Coupled Device
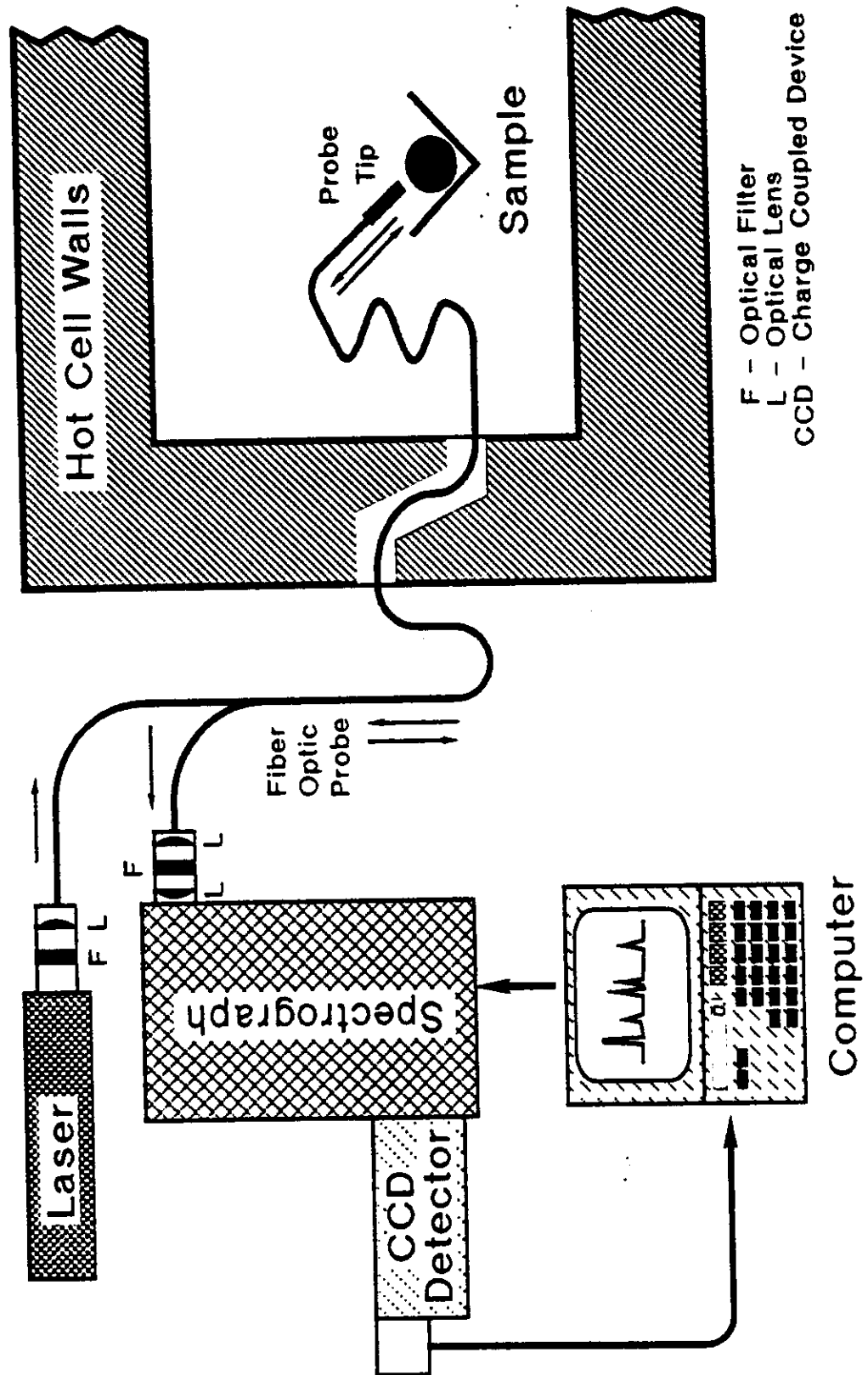
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7.0 DESCRIPTION OF TEST

The hot cell test bed and developmental effort supports applications at Hanford which lead to ultimate application of remote analysis in-situ. Tank Waste Remediation Systems characterization efforts center around the desire to reduce the cost of core sampling of the waste tanks. In addition, short term efforts are focused on the need to carry out direct ferrocyanide salt speciation and quantitation to help in the resolution of the USQ's. The ultimate goal is in-situ characterization developed in a stepwise fashion through the hot cells.

The primary driver for characterization work within the laboratory is to provide data for tank waste remediation actions. This characterization work supports: 1) processing requirements and 2) resolution of safety questions. A portion of this testing and application will be directed to quantitation and development of detection limits in the hot cell to effectively support ferrocyanide sample screening. This work will be further verified by comparison with laboratory data generated during conventional characterization of the ferrocyanide tanks.

This test examines a small subset of all possible types of remote Raman spectroscopy available. Several probe configurations will be examined, as well as different excitation sources. Because of sensitivity constraints for ferrocyanide analysis, a dispersive Raman instrument has been selected. For application to other known analytes near infrared Fourier Transform Raman spectroscopy may be more aptly suited. A list of possible technologies and those being examined are provided in Table 7.1.

Table 7.1 - Remote Raman Configuration.

Instrumental Components	Options	Components Examined in this Evaluation
Spectrometer/ Interferometer	Dispersive	X
	Fourier Transform	
Detector	CCD/Silicon	X
	Germanium	
Probe	Tapered 2-fibers	X
	N around 1 (N = 6, 18, 36 etc.)	X
	2 fiber probe with focusing optics	
Laser source	Diode	X
	Nd:YAG	
	Argon ion	
Software	Custom designed software	X
	Vendor supported standardized software	X

7.1 TEST SUBJECT

Extruded segments of waste, about 48 cm (19 inches) in length, are supplied to the 222-S Laboratories by core drilling operations at Tank Farms. This waste varies in consistency from slurries or extremely wet solids to peanut butter and hardened sludge. Dry crystalline solids are anticipated to be received from rotary coring operations. Occasionally, these waste segments "vary" throughout a single segment. When this occurs, the segment may be divided into facies which are analyzed separately (Winters 1990, Hill 1992). (See also Figure 5-1). Ferrocyanide tank segments are currently being analyzed as segments divided into quarters or into facies, as appropriate. Other SST's and tanks in which all materials are expected to be similar throughout are composited with contiguous materials. These composite samples are subsampled or submitted directly for analysis depending on the concerns or material expected in a given tank. Generally, when major constituents are of concern or tanks are expected to be stratified as in the case of ferrocyanide safety tanks samples, efforts concentrate on analysis of several subsections within a segment. Conversely, samples received for analysis of minor components require processing of larger sample sizes and often necessitate core compositing.

The 222-S Laboratory plans to characterize samples from two ferrocyanide tanks during campaigns in 1993. These tanks are 241-T-107 and 241-C-111. In addition, archived material taken from the auger sample of BY-104 will be examined.

Waste from tank T-107 were extruded in the hot cells at the 222-S Laboratory during the months of February and March 1993. Some of this sample will be archived in the hot cells, where preliminary spectral data of the extruded material will be made. Waste samples from tank C-111 are expected to arrive at the 222-S Laboratory facility later in FY '93. If a spectrometer is available during the time these cones are processed through the hot cell, samples will be scanned and species will be documented by vertical position on the extruded segments.

Both T-107 and C-111 are ferrocyanide watch list tanks. Cores will be taken from T-107 and C-111. Cores taken from tank T-107 are expected to consist of three and one quarter segments. Cores from tank C-111 will consist of one and one quarter segments.

The constituents and concentrations of Raman active analytes and major elements of interest are provided in Table 7.2 for both T-107 and C-111, based on expected compositions, and in Table 7.3 for analyzed tank waste samples taken from BY-104. Both tanks contain wastes of similar composition. There is an appreciable amount of tributyl phosphate expected to be present in samples taken from T-107. Acetate is also expected in C-111 waste samples in a maximum concentration of 1.34 mole/liter. (Hill 1992)

Table 7.2 - Expected Tank Contents of T-107 and C-111.

Analyte	Tank	Concentration
NO_3^-	T-107, C-111	7.3 moles/liter
NO_2^-	T-107, C-111	0.9 moles/liter
ZrO_2	T-107	0.15 moles/liter
CO_3^{2-}	T-107, C-111	0.65 moles/liter
PO_4^{3-}	T-107, C-111	0.3 moles/liter
SO_4^{2-}	T-107, C-111	0.085 moles/liter
Fe	T-107, C-111	0.03 moles/liter
CN^-	T-107, C-111	0.24 moles/liter
CH_3COO^-	T-107, C-111	1.34 moles/liter

Table 7.3 BY-104 Laboratory Analysis.

Analysis	Expected species	Result $\mu g/g$
TOC	Unknown	9,100 ± 300
TIC	CO_3^{2-}	19,000 ± 200
Total cyanide (modified)	$Fe(CN)_6^{4-}$ CN^-	69 ± 7
Al-ICP	$Al(OH)_3$	80,000
Fe-ICP	$Fe(CN)_6^{4-}$ $FeO(OH)$	7,000
P-ICP	PO_4^{3-}	3,000
Cr-ICP	CrO_4^{2-}	14,000
NO_2^--IC	$NaNO_2$	11,900 ± 1,000
NO_3^--IC	$NaNO_3$	49,000 ± 1,200
$PO_4^{3-}-IC$	$BiPO_4$ Na_3PO_4	5,780 ± 220
$SO_4^{2-}-IC$	Na_2SO_4 $SrSO_4$	26,500 ± 1,700

7.2 TEST ENVIRONMENT AND FACILITIES

Operations will be performed in the 222-S cubicle facilities by Westinghouse Hanford Processing and Analytical Laboratories personnel. The extrusion portion of this operation will be performed in the 1E-2 cubicle. After the segments have been extruded and the initial sampling has been completed, the segments will be placed into tared and numbered jars. The jars will then be transferred to the 1E-1 cubicle for homogenization and further sample breakdown and archiving.

Sample screening will proceed during extrusion or after archiving. All scanning activities occurring during extrusion and processing of waste samples should proceed within a suggested 30 minute time frame in order not to interfere with sample processing schedules and to protect sample integrity. A checklist of required spectra for each tank and individual objectives are provided in Table 7.4. Surrogate samples were selected to examine each of three separate flowsheet ferrocyanide compositions. Specifically, CJ-93-B is an In-Farm sludge, CJ-95-B is an early In-Farm formula and CJ-102-B is U Plant composition (Bechtold 1992). Each sample will be analyzed at least three times at different probe locations on the sample.

Table 7.4 - Spectra Required for Surrogates and Tank Samples by Analyte.

Analyte	Expected Species	Pure Reagent Spectra Archived	Surrogate in which analyte is expected	QA for Tanks Analyzed		
				BY-104	T-107	C-111
NO_3^-	$NaNO_3$ $SrNO_3^-$	Y	CJ-93-B CJ-95-B CJ-102-B	QualSpec triplicate	QualSpec triplicate ExtStand	QualSpec Homogeneity StandardAdd ExtStand
NO_2^-	$NaNO_2$	Y	N.A.	QualSpec triplicate	QualSpec SemiQuant triplicate ExtStand	QualSpec SemiQuant Homogeneity ExtStand
PO_4^{3-}	Na_3PO_4	Y	CJ-93-B CJ-95-B CJ-102-B	QualSpec triplicate	QualSpec SemiQuant triplicate ExtStand	QualSpec SemiQuant Homogeneity ExtStand
CO_3^{2-}	Na_2CO_3	Y	N.A.	QualSpec triplicate	QualSpec SemiQuant triplicate ExtStand	QualSpec SemiQuant Homogeneity ExtStand
SO_4^{2-}	Na_2SO_4	Y	CJ-93-B CJ-95-B CJ-102-B	QualSpec triplicate	QualSpec SemiQuant triplicate ExtStand	QualSpec SemiQuant Homogeneity StandardAdd ExtStand
$Cs_2NiFe(CN)_6$		Y	N.A.	QualSpec triplicate	QualSpec SemiQuant triplicate ExtStand	QualSpec SemiQuant Homogeneity StandardAdd ExtStand
$Na_2NiFe(CN)_6$		Y	CJ-93-B CJ-95-B CJ-102-B	QualSpec triplicate	QualSpec SemiQuant triplicate ExtStand	QualSpec SemiQuant Homogeneity StandardAdd ExtStand
$K_4Fe(CN)_6$		Y	CJ-93-B CJ-95-B CJ-102-B	QualSpec triplicate	QualSpec SemiQuant triplicate MatrixSpF ExtStand	QualSpec SemiQuant Homogeneity MatrixSpF StandardAdd ExtStand
$K_3Fe(CN)_6$		Y	N.A.	QualSpec triplicate	QualSpec SemiQuant triplicate ExtStand	QualSpec SemiQuant Homogeneity StandardAdd ExtStand

QualSpec = Qualitative Spectra will be obtained
triplicate = analysis will be performed in triplicate
SemiQuant = Concentration will be estimated by ratioing to NO_3
Homogeneity = Spectra will be obtained down segment and across and compared
StandardAdd = Standard Addition will be performed for comparison with semi-quantitative data and laboratory results.
ExtStand = A spike of a known amount of perchlorate will be mixed into sample and used to ratio with analyte response factors.
MatrixSpF = Percent recovery of a known amount of ferrocyanide added to the sample matrix will be calculated.

7.3 QUALIFICATION PLAN

As part of this effort an extensive qualification plan will be prepared to establish the validity and limitations of data obtained from the remote Raman screening system for quantitative analysis of ferrocyanide species in tank wastes. This qualification plan will be divided into three parts: a spectrometer performance check, operations check, and chemical speciation and software qualification.

The spectrometer performance check will be based on the principles described in American Society for Testing and Materials (ASTM) Standard Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers (E-932-83). This standard assumes the use of proper instrumentation for the characterization task and that instrumental factors responsible for inaccuracies in dispersive spectroscopy are resolution, linearity, stray radiant energy, and cell constants (in conventional spectroscopic systems). Inaccuracies stemming from cell constant parameters may be translated to irreproducibility of sample probe interface positioning in fiber optic remote spectroscopy. The ASTM standard requires measurement of ambient temperature, response time, signal-to-noise ratio, and mechanical repeatability. An initial performance check on wavenumber accuracy and precision is also required using a neon standard. Optimization of spectral slit width will be performed at each setup according to protocols established by FSU (WHC 1992) and a white light spectrum will be generated and archived.

Calibration will be performed using analyzed standards that are traceable to National Institute of Standards and Technology (NIST) traceable cyanide and iron content. These standards will be made in 99.9% purity sodium nitrate salt matrices. An independent check standard will be constructed in the same matrix and percent recovery and photometric precision will be reported on the check standard. This calibration will be performed prior to each system setup.

A check for variations over small sample areas will be performed over an approximately 5 cm^2 surface area of a sample (freshly extruded, if available). Spectra will be obtained from ten different probe positions in this area. The collected spectra will be treated statistically to quantify the extent of variation. However, small sample area variances thus observed appear to result from pure photon counting statistics and may be eliminated by spectral summing.

Data obtained after the system has been calibrated for ferrocyanide will be recorded along with percent recovery on check standards and blank determinations. A spectrum of a surrogate with an analyzed concentration of cyanide exceeding 0.4 weight percent will be obtained. This will provide proof that ferrocyanide species can be found in a matrix similar to the tank wastes with the system configuration used at the time of analysis.

Finally, a matrix spike for ferrocyanide will be performed and percent recovery of spike material will be recorded for an approximately 5 mL subsample of real tank wastes, depending on the amount of ferrocyanide found in the real waste material. In the event no ferrocyanide is found in the real waste materials, the simulant and real waste material may be spiked with ferrocyanide, as well.

Archived spectra will continue to be added to the system memory and qualitative analysis will be provided of those species that have archived spectra available. Target anions such as nitrates, nitrites, sulfates, phosphates, and carbonates will be included as primary screening points.

Software qualification will include peer review of chemometrics data manipulations and verification of photometrically determined wavenumber precision and accuracy with neon and probe standards.

Finally, extensive documentation requirements will be required for all spectra collected. Important parameters which must be monitored and controlled should include but not be limited to: laser source frequency and power, spectrometric slit widths, detector integrating time, and fiber optic characteristics.

7.4 TEST DATA AND COMPARISONS

A complete list of data analysis parameters is provided in Table 7.5 based on observations required from the qualification plan. These parameters will be monitored and data comparisons will be documented to support viability of this analysis in the operations environment.

On initial deployment of the remote Raman screening instrument into the hot cell, spectra will be obtained of BY-104 and T-107 archived wastes. Raw data or uncalibrated spectra will be obtained and normalized to the nitrate peak near $1,000$ cm^{-1}, as well as, to the Rayleigh line in the event that nitrate concentrations should vary down the segment length. The oxyanion concentrations will then be estimated based on nitrate concentration as provided by ion chromatographic (IC) analysis. A semi-quantitative analysis for ferrocyanide species will be performed by ratio to nitrate, if the potassium ferrocyanide species is detected in the sample. This ratio will be based on instrument response factors for analytes of interest as compared to the nitrate response factor. Oxyanion concentrations obtained will be compared to results obtained from IC.

A third set of spectra will be obtained during extrusion of C-111 material to demonstrate detection of tank waste inhomogeneities directly after extrusion. At least ten sets of spectra will be obtained around the circumference of the segment. Spectra obtained down the length of the segment will be obtained at positions at least 2 inches apart.
A comparison of homogeneity will be made based on the spectra obtained.

Prior to final hot cell deployment and ferrocyanide quantitative analysis, a qualification check will be performed on the hot cell system. Included in this system performance optimization, calibration using solid $NaNO_3$ salt standards and check standards and quantitative analysis of a surrogate and at least one of the previously analyzed real tank waste materials.

Table 7.5. Experimental Parameters.

Testing Phase	Qualification Catagory	Parameter	Monitoring Method
Initial testing and optimization	Spectrometer performance	Resolution	Plot int. vs. resolution
		Linear dispersion	Calibration with neon source
		Stray radiant energy	Radiation source response
			White light response
		Mechanical repeatability	Scanning to identical spectrometer position repeatability
	Species identification	Photometric accuracy	-Check laser frequency -Run pure standards for comparison -Determine instrumental limit of detection
Weekly system checks	Operations check software and speciation check	Photometric accuracy	-Simulants determinations -Matrix spikes -Signal to noise determinations
Daily operation checks	Operation check	Response time	Document acquisition time
		Ambient temperature	Document temperature for comparison to previous results
		Laser frequency and power	Document in instrument logbook for performance history
	Species identification algorithm and software check	Sample variance	Sample averaging over small areas.
		Photometric accuracy	-Independent concentration and species check standard. -Blank determinations.

8.0 EXPECTED RESULTS

The current detection limit for analysis of solid ferrocyanide salts in nitrate salt matrices under ideal conditions (i.e. calibration via signal acquisition on a spun sample) is 0.6 weight percent ferrocyanide (WHC 1992). Recent analyses of BY-104 materials indicate concentrations of cyanide to be only 69 μg per gram of sample equivalent to 1 x 10^{-3} weight percent $Fe(CN)_6^{4-}$. Process knowledge (Hill 1992) indicates that tanks T-107 and C-111 should contain 0.03 moles of Fe per liter of waste. Assuming a waste density of 1.4 g/mL, and assuming all iron is in the form of ferrocyanide salt, this translates to a maximum concentration of 0.5 weight percent ferrocyanide possible in the tanks. This concentration is below the detection limit for the instrument as described by FSU (WHC 1992). However, efforts are continuing to improve detection limits below those determined by use of higher energy laser sources and more efficient collection probe configurations. In the event that ferrocyanide species are not determined in those tank samples, simulants with ferrocyanide concentrations exceeding 0.5 weight percent will be analyzed in the hot cell to determine the capability of the system to detect ferrocyanide in the hot cell environment. This protocol serves to verify the ability of the instrument to detect levels of ferrocyanide above 0.5 weight percent while assuring against false negative results. Continued work will progress with examination of laser sources and probes which will increase sensitivity.

Additional analytes expected in these wastes are similar to those obtained from BY-104 which are listed in Table 7.1.

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9.0 SAFETY

No new kinds of waste will be generated with this test plan.
Disposal of waste materials will be performed per approved procedures. All
materials contacting HLW are handled as RMW (WHC 1990).

All activities involving use of lasers have been approved by a WHC laser
safety officer on the attached job safety analysis and comply to the
requirements provided in the latest revision of WHC-CM-4-3, standard W-8..
Employees involved with laser systems have been trained on their appropriate
use and safety features have been engineered into the system to ensure laser
safety classification I, the lowest hazard class, applies.

A job safety analysis has been completed and is included for operation
of the Raman system at the hot cells in Appendix A. Other specific laboratory
safety issues related to operation of the hot cells are addressed in standard
laboratory operating procedures.

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10.0 LABORATORY PROCEDURES AND QUALITY ASSURANCE

The following procedures will be observed during core segment load in and extrusion of tank wastes in the 222-S Laboratory 1E-2 hot cells:

LT-150-101	Core Segment Receipt and Preparation
LT-549-101	Core Segment Extrusion
LT-547-102	Homogenization and Homogenized Segment Sampling
LT-549-103	Core Compositing and Sampling

Analysis that will be performed in support of tank waste characterization and comparison with data collected during waste screening are as follows:

LA-344-105	Total Organic Carbon (TOC) Analysis
LA-505-158	Inductively Coupled Plasma (ICP) Metals Analysis
LA-505-151	ICP Metals Analysis
LA-533-105	Anions by IC
LA-695-101	Cyanide Analysis by Distillation and Spectrophotometry
LA-622-102	Carbonate Analysis by Coulometric Titration

The sampling and analysis work performed for this test plan shall conform to Analytical Chemistry Services Laboratories Quality Assurance Plan WHC-SD-CP-QAPP-001 (WHC 1991) and the Quality Assurance Project Plan for the Chemical Analysis of Highly Radioactive Mixed Waste Samples in Support of Environmental Activities on the Hanford Site WHC-SD-QAPP-002 (Moss 1992).

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15. Five sets of averaged spectra will be collected down the length of the segment at approximately 2 inch intervals and these measurements will be performed in triplicate.

16. All spectra obtained after extrusion will be ratioed to the nitrate and Rayleigh line and a comparison will be made from the segment profile.

17. A calibration for ferrocyanide will be performed using potassium ferrocyanide in $NaNO_3$ of at least 99.9% purity. Five standards ranging from 0.2 weight percent to 2.0 weight percent potassium ferrocyanide will be used in calibration.

18. A limit of detection will be calculated as the inverse of the calibration curve slope times 3 times root mean square noise.

19. Spectra will be obtained on selected BY-104, T-107, and C-111 samples. Potassium ferrocyanide content will be determined from these spectra using the calibration curve generated in step 18. System stability will be measured by determination of concentration of ferrocyanide.

20. Results will be compared to results calculated based on nitrate ratioing and an analyzed nitrate concentration provided from IC determinations.

11.0 TEST PROCEDURE

1. The system will be shipped and optimized in the 222-SA Process Chemistry Laboratory.

2. A preliminary check of wavenumber precision and accuracy will be performed with a neon source or sodium nitrate.

3. Spectra of at least two ferrocyanide surrogates with analyzed concentrations exceeding 0.4 weight percent cyanide will be stored for qualitative analysis. These spectra will include at least one slurry and one dried solids spectrum from each surrogate. Dried solids will be sent to PNL for peer analysis.

4. Spectra of sodium nitrate, sodium nitrite, trisodium phosphate and potassium ferrocyanide will be obtained.

5. The spectrometer will be transferred to the hot cell after inspection by laboratory HPTs, demonstration that the instrument will function in a 100mR/hr gamma field, and written release agreements are in place.

6. Calibration and optimization of the Dispersive Raman System will be performed by Florida State University prior to hot cell analysis. Details of calibration will be documented at that time.

7. A dark and white light spectrum will be obtained and stored as obtained in the hot cell environment.

8. Surrogates previously analyzed in step 3 and stored T-107 materials will be loaded into the 1E-2 hot cell for comparison with real ferrocyanide tank wastes.

9. Spectra will be obtained of T-107 wastes, BY-104 wastes, and surrogates, and these spectra will be stored.

10. Rayleigh line intensity will be recorded for each spectrum obtained.

11. All oxyanion and ferrocyanide information and respective Raman intensities of all materials will be observed and recorded in a controlled laboratory notebook.

12. All oxyanion and ferrocyanide data will be ratioed to the nitrate and Rayleigh lines.

13. Observation of spectral variations from probe movement will be made. Methods of cleaning the probe surface will be investigated.

14. During extrusion of C-111 tank wastes, spectra will be collected and averaged over 10 positions across the circumference of the extruded sample.

12.0 REPORTING

Analytical results will be documented in controlled laboratory notebooks. A final report will be cleared for public release along with the qualification plan for validation of the Raman screening system.

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13.0 REFERENCES

Bechtold, D. B., C. J. Jurgensmeier, 1992, *Report of Beaker Tests of Ferrocyanide Scavenging Flow Sheets*, WHC-SD-WM-TRP-071, Revision 0, Westinghouse Hanford Company, Richland, Washington.

Beck, M. A., 1992, *Waste Tank Characterization Plan for Sampling and Analysis of Augered Surface Samples from Tanks containing Ferrocyanide Wastes*, WHC-SD-WM-TP-114, Revision 2, Westinghouse Hanford Company, Richland, Washington.

Hill, J. G., 1992, *Tank Waste Remediation System Tank Waste Characterization Plan*, WHC-SD-WM-PLN-047, Revision 1, Westinghouse Hanford Company, Richland, Washington.

Moss, S. S., 1992, *Quality Assurance Project Plan for the Chemical Analysis of Highly Radioactive Mixed Waste Samples in Support of Environmental Activities on the Hanford Site*, WHC-SD-QAPP-002, Revision 0, Westinghouse Hanford Company, Richland, Washington.

WHC, 1992, *Detection and Quantitative Analysis of Ferrocyanide and Ferricyanide*, WHC-SD-TD-RPT-003, Revision 0, Westinghouse Hanford Company, Richland, Washington.

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WHC, 1990, *Routine Cubicle Waste Loadout*, LO-100-103, Westinghouse Hanford Company, Richland, Washington.

Winters, W. I., L. Jensen, L. M. Sasaki, R. L. Weiss, J. F. Keller, A. J. Schmidt and M. G. Woodruff, 1990, *Waste Characterization Plan for the Hanford Site Single-shell Tanks*, WHC-EP-0210, Revision 1-3, Westinghouse Hanford Company, Richland, Washington.

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APPENDIX A

JOB SAFETY ANALYSIS

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JOB SAFETY ANALYSIS	Job Description Operation of Diode Laser in 1E-2 Hot Cell		JSA Number PCL 92-05	
	Component Process Chemistry Laboratories		Building/Area 222-S 200W	

Reviewed By INDUSTRIAL SAFETY AND FIRE PROTECTION	Prepared By Beverly A. Crawford		Date 08/11/92
Date 8/24/92 Initials aCWZ	Review Dates		

SAFETY EQUIPMENT REQUIRED	TOOLS AND EQUIPMENT REQUIRED	JOB PREPARATION
Hot Cell	Diode Laser Fiber Optic	Review procedure steps for turning on laser.
	HAZARDOUS MATERIALS	RELATED REQUIREMENTS
	radioactive tank wastes	Radiation Work Procedure Yes [X] No [ ] Nuclear Safety Specification Yes [ ] No [X]

JOB STEP	HAZARD	HAZARD CONTROL AND PROTECTIVE EQUIPMENT
1.Turn laser on	None	
2.Check to see that light is being delivered through fiber optic by observing Raman instrument response.	Light exposure to eyes	Turn system off if beam is not totally enclosed. Do not open system while in operation. Do not attempt to check light transmission through fiber with eyes.
3.Place fiber optic in sampling position to sample	None	

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WHC-SD-WM-TP-157, Rev. 0

List attachments.
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Date Release Required

Title PRELIMINARY EVALUATION OF RAMAN SPECTROSCOPY FOR THE HOT CELL

Unclassified Category UC-

Impact Level 4

New or novel (patentable) subject matter? [X] No [] Yes
If "Yes", has disclosure been submitted by WHC or other company?
[] No [] Yes Disclosure No(s).

Information received from others in confidence, such as proprietary data, trade secrets, and/or inventions?
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Author/Requestor (Printed/Signature)
B. A. Crawford   *(signature)*   **Date** 4/6/93

Intended Audience
[] Internal [X] Sponsor [] External

Responsible Manager (Printed/Signature)   **Date**
J. R. Jewett   *(signature)*   4/6/93

Date Cancelled	Date Disapproved

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DISTRIBUTION SHEET

To: Characterization & Safety Technology	From: Process Chemistry Laboratory	Date: April 6, 1993

Project Title/Work Order:

PRELIMINARY EVALUATION OF RAMAN SPECTROSCOPY FOR THE HOT CELL

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TFIC	R1-28	X		
ECM	L8-14			X
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IRR	R1-08			X
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